

IMMOBILIZATION OF NANOSCALE ZERO-VALENT IRON (NZVI) ONTO ELECTROSPUN NANOFIBER MEMBRANE FOR GROUNDWATER REMEDIATION

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the degree of

Doctor of Philosophy

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Jiawei Ren, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology at the University of Technology Sydney. This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution.

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LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Processes
ATR-FTIR	Attenuated Total Reflectance– Fourier Transform Infrared Spectroscopy
ATRP	Atom Transfer Radical Polymerization
BET	The Brunauer-Emmett-Teller
BSA	Bovine Serum Albumin
CA	Contact Angle
Cd (NO ₃) ₂	Cadmium Nitrate
–COOH	Carboxyl Group
CT	Tetrachloride
Cu (NO ₃) ₂	Cupric Nitrate
DI	De-Ionized
DMF	N, N-Dimethylformamide
DO	Dissolved Oxygen
EDX	Energy Dispersive X-Ray Spectroscopy
ENM	Electrospun Nanofiber Membrane
EPA	Environmental Protection Agency
Fe(II)	Ferrous Ions
Fe(III)	Ferric Ions
FeCl ₃	Ferric Chloride
FeSO ₄ ·7H ₂ O	Sulphate Heptahydrate
GO	Graphene Oxide
H ₂ O ₂	Hydrogen Peroxide

ISCO	In-Situ Chemical Oxidation
IWA	In-Well Aeration
MF	Microfiltration
MW	Molecular Weight
NaBH ₄	Sodium Borohydride
NaOH	Sodium Hydroxide
NOMs	Natural Organic Matters
nZVI	Nanoscale Zero-Valent Iron
P&T	Pump And Treat
PAA	Polyacrylic Acid
PAN	Polyacrylonitrile
PCBs	Polychlorinated Biphenyls
PCE	Tetrachloroethylene
PGMA	Poly(Glycidyl Methacrylate)
PRB	Permeable Reactive Barrier
PSD	Pore Size Distribution
PVA	Polyvinyl Alcohol
PVDF	Polyvinylidene Fluoride
RH	Relative Humidity
SEM	Scanning Electron Microscopy
TCD	<i>Tip-To-Collector-Distance</i>
TCE	Trichloroethylene
TEM	Transmission Electron Microscopy

TGA	Thermogravimetric Analysis
TiO ₂	Titanium Oxide
UF	Ultrafiltration
XRD	X-Ray Diffraction
α -Fe ₂ O ₃	Hematite
α -FeOOH	Goethite

ABSTRACT

Nanoscale zero-valent iron (nZVI), as a promising material, has been widely used in groundwater remediation. However, individual nZVI particles are prone to agglomeration and hence sediment in the water environment, which reduces the reactivity of nZVI as well as its performance in contaminant removal. Membrane-supported nZVI can both avoid nZVI agglomeration for better reactivity and recycle nZVI/contaminants to lower the risk of secondary pollution.

In this study, a new approach that combines nZVI with electrospinning technology has been put forward to obtain the membrane-supported nZVI. First, we developed a polyacrylic acid - polyvinyl alcohol (PAA-PVA) electrospun nanofiber membrane. The results indicate that nZVI particles were successfully immobilized on the membrane and had excellent removals to methylene blue and Cu (II) ions at 94% and 83.6% respectively. Subsequently, a “robbing behaviour” was observed during the nZVI immobilization. The robbing behaviour can significantly reduce the number of nZVI particles immobilized onto the membrane and hence weaken the performance of mitigating contaminated water. To minimize the undesirable effect of robbing behaviour, we developed a dipping method that enables exposure of enough free Fe (II) as electron acceptors to the Fe (II)-complexed PAA-PVA membrane for the subsequent reduction. The results shows that the membrane with dipping can immobilize more than 1.7 times the weight percentage of nZVI particles for the membrane without dipping. However, we found that the developed PVA-PAA-nZVI composites had a low mechanical strength after undergoing multiple reduction by NaBH₄ and membrane mechanical strength is a critical property for a long-term operation and the regeneration of nZVI membranes. Therefore, a high molecular weight dual-

crosslinking method was investigated to improve the mechanical strength of polymeric electrospun nanofiber membranes.

Alternatively, we examined to fabricate a polyvinylidene fluoride - graphene oxide (PVDF-GO) nanofiber membrane composite for nZVI immobilization. The addition of GO into PVDF nanofibers can both increase the hydrophilicity to improve membrane flux and offer –COOH as a binder to immobilize nZVI particles. PVDF-GO-nZVI membranes with different GO loadings (0%, 0.5%, 1%, 3% of PVDF) were tested with two typical nZVI-targeted contaminants (Cd(II) and trichloroethylene (TCE)) via gravity-driven membrane filtration. The results show that membrane with 1% GO had the best nZVI distribution against the aggregation and a better performance in both Cd removal (100%) and TCE removal (82%).

To sum up, the electrospun nanofiber membrane is a very suitable material for nZVI immobilization and the developed nZVI-immobilized electrospun nanofiber membrane composites had a great potential in groundwater remediation.

Keywords: nZVI; Electrospun nanofiber membrane; Membrane-supported nZVI; Groundwater remediation; Gravity-driven membrane filtration; Immobilization; Nanoparticles; Electrospinning; Composites

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